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Effects of pH and Salinity on Copper, Lead, and Zinc Sorption Rates in Sediments from Moreton Bay, Australia

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The partitioning of trace metals between the solid and dissolved phases plays a critical role in regulating metal availability in natural waters. Sorption studies typically have shown that sorption of trace metals by soils and sediments is initially rapid (Honeyman and Santschi 1988; Comber et al. 1996; Liu and Huang 2003), followed by continued sorption over an extended time period (up to 100 days) (Comber et al. 1996). Although information is available for the effects of pH and salinity on equilibrium metal sorption by soils and sediments, corresponding information on sorption rates, particularly for estuarine sediments, is limited. This is particularly the case for estuarine sediments of the Moreton Bay region, south-east Queensland, Australia, where increased urbanization and surface water runoff has increased metal loadings to the region (Burton et al. 2004). To evaluate the environmental risk posed by increasing metal inputs to presently uncontaminated sediment-water systems, it is important to understand if the added metals are rapidly removed from solution through sorption to the sediments, or if they remain in solution and therefore capable of being transported within the water column. The objective of this study was to examine the influence of pH and salinity on copper (Cu), lead (Pb) and zinc (Zn) sorption rates by two sediments with contrasting physical and chemical properties.

MATERIALS AND METHODS

Samples of two estuarine sediments (MM and CS) that exhibited contrasting chemical and physical properties (Table 1) were collected from the western side of Moreton Bay, south-east Queensland, Australia (S27° 38.332’ E153° 18.769’). Samples were collected from the oxic layer (0-5 cm depth interval) at the sediment-water interface. These sediments are exposed daily to atmospheric oxygen during falling tides, and are overlain by oxic marine quality water during rising tides (>90% dissolved oxygen saturation, Moss and Cox 1999).

Sorption kinetic studies were conducted at 3 initial pH values (pH 4, 6 and 8) and 2 salinities (5 and 30 parts per thousand). One litre of artificial seawater (Greenberg et al. 1992) was added to glass reactors, and spiked to achieve a final Cu, Pb and Zn concentration of 16 mg/L, 16 mg/L and 32 mg/L respectively (as

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Table 1. Selected initial properties of the FS and MM sediments (Rayment and Higginson 1992).

Sediment	pH	Sand (%)	Org. C (%)	CEC ($cmol_c$/kg)	Total metal concentration (mg/kg)		
					Cu	Pb	Zn
FS	7.5	85	2.6	7.9	0.42	0.91	0.08
MM	7.5	70	4.8	15.2	0.57	0.77	0.81

nitrate salts). Twenty-five grams of sediment were added to the spiked solution, and the sediment was maintained in suspension by continuous stirring. Continuous stirring simulated resuspension of benthic sediment due to tidal-, wind- or storm-induced water movement, and to minimize time-dependent transport processes on metal sorption kinetics. After 0.17, 0.5, 1, 3, 6, 24, 48 and 120 hours (h), 50 mL of suspension were removed using a plastic syringe, then centrifuged (2 min at 4000 rpm) and filtered (0.45 μm). Twenty mL of filtrate were acidified with nitric acid to achieve a final pH of <2, and stored in polycarbonate vials prior to Cu, Pb and Zn analysis by atomic absorption spectrometry (AAS; Varian SpectrAA Atomic Absorption Spectrometer).

The rate constant (k) was estimated by fitting a first-order kinetic equation to the experimental data using non-linear regression analysis (SPSS Inc., Illinois, USA). The aqueous metal concentration at time t can be expressed as (Sparks 2003):

$$c(t) = c_e + (c_0 - c_e)e^{-kt} \tag{1}$$

where c_e is the aqueous metal concentration at equilibrium (mg/L), c_0 is the aqueous metal concentration (mg/L) at $t = 0$, k is the sorption rate constant (1/h), and $c(t)$ is the aqueous metal concentration (mg/L) at $t > 0$, and t is time (h).

The distribution coefficient (K_D) was calculated after 180 minutes reaction time (since after this time no significant changes in metal sorption were observed) as:

$$K_D = S \div c_a \tag{2}$$

where K_D is the distribution coefficient (L/kg), S is the sorbed metal concentration (mg/kg) and c_a is the metal concentration in the aqueous phase (mg/L).

RESULTS AND DISCUSSION

Measured and fitted Cu, Pb and Zn sorption kinetics by the two sediments are presented in Figure 1, 2 and 3, respectively. Sorption of the three metals followed a similar pattern; sorbed concentrations increased rapidly over the initial 10-60 minutes, and then remained relatively constant. More than 90% of the added Cu and Pb was sorbed by the sediments within 60 minutes of commencing the experiment, at both pH 6 and 8; however, only between 30-60% of the applied Cu and 40-90% of the applied Pb was sorbed at pH 4. Zinc sorption was found to be approximately 30, 70 and >95% at pH 4, 6 and 8 respectively, for both sediments.

Metal sorption (due to both adsorption and precipitation mechanisms) observed in this study was consistent with published literature, in that sorption increased

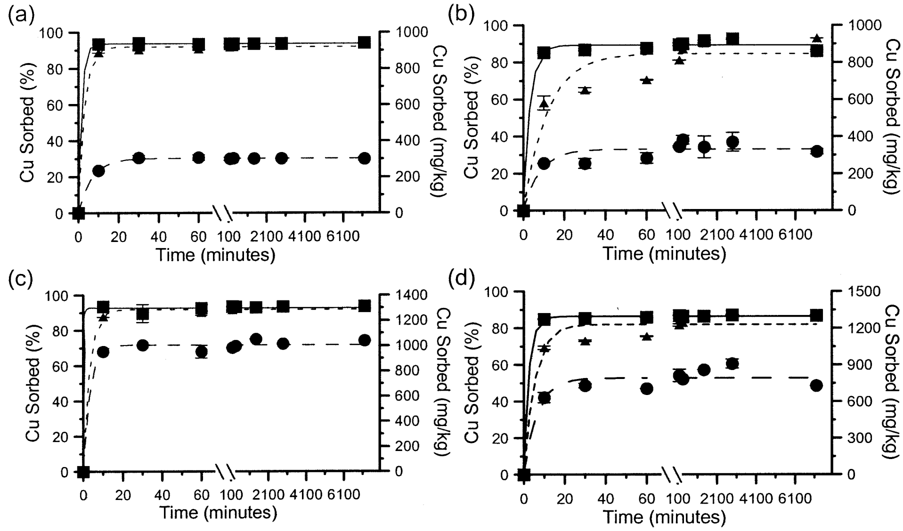

Figure 1. Measured (● pH 4, ▲ pH 6, ■ pH 8) and fitted (long dash pH 4, short dash pH 6, solid line pH 8) Cu sorption kinetics for FS and MM. Data was fitted using Equation 1. (a) 5 ppt FS; (b) 30 ppt FS; (c) 5 ppt MM; and (d) 30 ppt MM.

positively with increasing pH (Kinniburgh et al. 1976). This can be attributed to (1) increased adsorption onto organic and mineral ion exchange sites created by deprotonation, (2) preferential adsorption as hydroxy-metal species by soil organic matter and/or hydrous iron and aluminium oxides (sesquioxides), and (3) homogeneous- and surface-precipitation of hydroxy-carbonate minerals.

Preliminary studies found that the CEC of both sediments was not significantly affected by pH, so preferential adsorption and precipitation reactions may explain the greater sorption with increasing pH observed in this study. The contribution of hydrous oxides to metal sorption was not evaluated in this study, but the higher organic carbon content and CEC of MM would encourage greater metal sorption relative to FS (Table 1).

The first-order model (Equation 1) adequately described the Cu and Pb sorption kinetics for both sediments ($r^2 > 0.90$); however, Zn was described less satisfactorily ($r^2 = 0.33$-0.99) (Table 2). Generally, the sorption rate constant (*k*) for Cu and Pb increased with pH, and decreased with increasing salinity (5 ppt versus 30 ppt). For example, *k* values for Cu sorption by FS at 5 ppt salinity were 9.06, 19.89 and 36.98 (1/h), and at 30 ppt were 7.58, 5.16 and 18.57 (1/h), at pH 4, 6 and 8 respectively. The increase in *k* with pH suggests that raising the pH increased the accessibility of potential sorption sites for the added metals, increased the number of potential metal sorption sites, increased the ability of the metals to be adsorbed, and/or caused rapid precipitation of amorphous Cu and Pb hydroxy-carbonate minerals. Of these possible reasons, the formation of hydroxy-metal complexes, and subsequent specific adsorption and/or surface precipitation

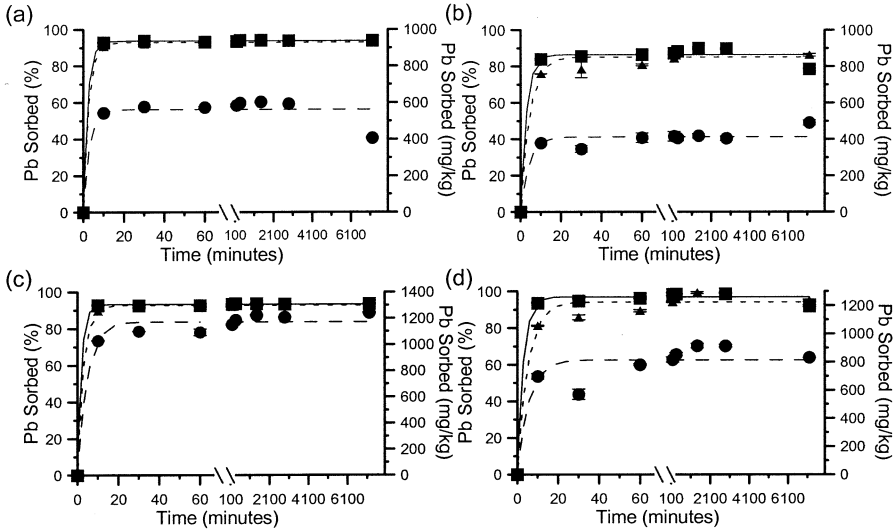

Figure 2. Measured (● pH 4, ▲ pH 6, ■ pH 8) and fitted (long dash pH 4, short dash pH 6, solid line pH 8) Pb sorption kinetics for FS and MM. Data was fitted using Equation 1. (a) 5 ppt FS; (b) 30 ppt FS; (c) 5 ppt MM; and (d) 30 ppt MM.

at nucleation sites, may be the more important mechanism causing increases in *k*. Hydrolysis constants (expressed as pK_a) for Pb, Cu and Zn are about 7.8, 8.0 and 9.0 respectively (Kinniburgh et al. 1976). Speciation calculations indicate that much of the metals would have existed primarily in hydrolysed forms for the pH 8 treatment (Figure 4). This may explain the near-complete sorption of all metals at pH 8. Furthermore, at pH 4, Figure 4 indicates that the added metals existed in their cationic form to a greater degree than at pH 6 and pH 8. This would result in considerable competition between the added metals and cations in background solution for the limited cation exchange sites. The lower *k* value at the high salinity (30 ppt) was also likely due to this increased competition between the added metals and the high concentration of cations in the artificial seawater (i.e. Ca, Mg, K and Na), in addition to a compression of the electrical double layer surrounding negatively charged surfaces. This effect has been commonly observed in unsaturated sediments such as soils (Naidu et al. 1994). Reduced sorption at higher salinity could also be attributed to decreases in the activity coefficient with increases in ionic strength. The formation of ion-pairs between trace metals and major seawater anions may also contribute to reduced sorption with increased salinity. The inorganic speciation of Cu, Pb and Zn in 5 ppt and 30 ppt artificial seawater (Figure 4) further highlights the importance of ion-pair formation, which shows that increasing salinity from 5 ppt to 30 ppt reduces the abundance of Cu^{2+}, Pb^{2+} and Zn^{2+} by approximately 10, 30 and 15%, respectively. The abundance of $CuOH^+$, $PbOH^+$ and $ZnOH^+$ (which may be specifically adsorbed to surface sites or precipitated as mineral species) is also reduced with increased salinity, due to the presence of metal-Cl^- and/or metal-CO_3^{2-} ion-pairs.

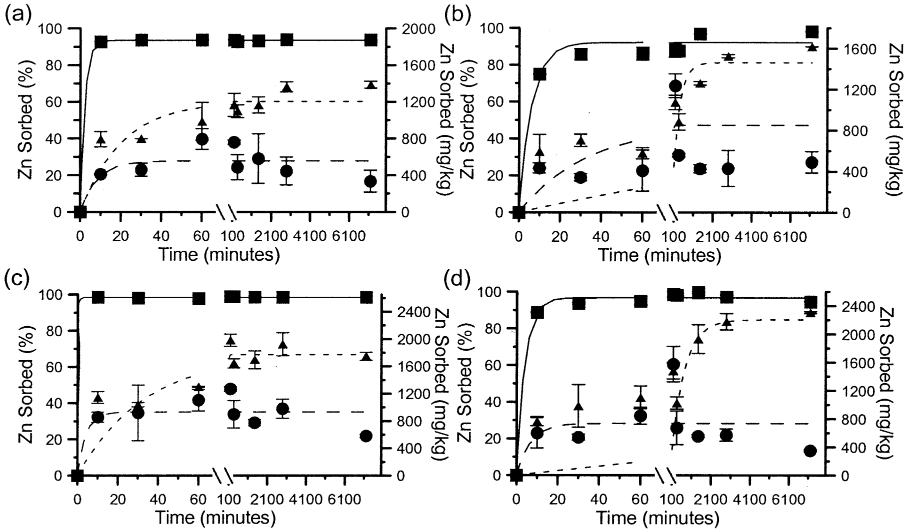

Figure 3. Measured (● pH 4, ▲ pH 6, ■ pH 8) and fitted (long dash pH 4, short dash pH 6, solid line pH 8) Zn sorption kinetics for FS and MM. Data was fitted using Equation 1. (a) 5 ppt FS; (b) 30 ppt FS; (c) 5 ppt MM; and (d) 30 ppt MM.

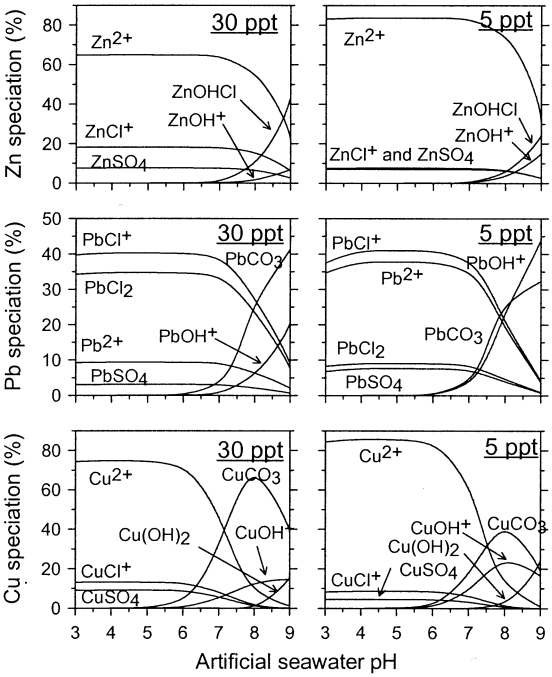

Figure 4. Aqueous speciation of Cu, Pb and Zn (total aqueous concentration = 0.02 m*M*) in artificial seawater with 30 ppt and 5 ppt salinity as calculated with the geochemical equilibrium program PHREEQC (Parkhurst 1995).

Table 2. Copper, Pb and Zn sorption rate constant (k) for each pH and salinity treatment calculated by Equation (1) for each sediment sample. All units in 1/h.

Metal	pH 4		pH 6		pH 8	
	5 ppt	30 ppt	5 ppt	30 ppt	5 ppt	30 ppt
Sediment FS						
Cu	9.1±0.3	7.6±3.1	19.9±2.6	5.2±1.8	37.0±7.7	18.6±3.9
Pb	20.4±2.4	14.7±2.5	22.6±2.6	13.2±0.8	28.0±2.4	21.0±9.5
Zn	7.4±6.7	1.8±2.6	3.0±1.3	0.2±0.1	28.3±2.8	9.8±2.3
Sediment MM						
Cu	17.6±3.9	9.3±2.8	18.3±2.3	10.8±2.6	165±4.3	24.1±0.4
Pb	12.5±2.5	10.7±5.4	20.5±1.9	11.7±2.3	31.6±6.0	20.1±5.5
Zn	15.0±18.5	9.0±15.8	1.8±0.8	0.1±0.1	149±43	14.9±1.8

Reported metal sorption rate coefficients obtained under varying pH and salinity conditions are scarce, and values vary widely depending on the sorbing media used (Gee and Bruland 2002). Jain and Sharma (2002) reported k values between 2.1 and 5.2 (1/h) for Cd sorption to freshwater sediments at pH 6.8, and Achterberg et al. (2002) reported $k = 4$ (1/h) for Cu sorption at pH 7.4. Lin and Juang (2002) found k for Zn and Cu to be 0.04 and 0.19 (1/h) at pH < 3 on a modified montmorillonite substrate. Chiron et al. (2003) reported k for Pb and Cu to be 4.02 and 1.92 (1/h), respectively, on grafted silica at pH 5.5.

The effect of pH and salinity on the distribution coefficient (K_D) was similar to that observed for k; i.e. K_D generally increased with increasing pH, and decreased with increasing salinity (Table 3). Except for pH 8 systems, K_D values decreased in the following order: Pb > Cu > Zn. This order for the lower pH treatments supports the contention that preferential sorption (possibly as hydroxy-metal species) and surface precipitation of hydro-carbonate minerals were important mechanisms affecting Pb, Cu and Zn sorption by these estuarine sediments. At pH 8, K_D values reflected near complete removal of all metals from solution, which may be largely attributed to homogeneous precipitation of hydroxy-carbonate minerals.

The values of K_D reported here (Table 3) were consistent with values in the published literature. Christensen et al. (2000) found that increasing pH from 5.5 to 8, increased K_D (expressed on $\log_{10}$ basis) for Cu from 2.31 to 3.36 L/kg, and for Zn from 0.86 to 3.26 L/kg, respectively. Comber et al. (1996) found Zn and Cu sorption by estuarine sediments tended to decrease with increasing salinity. Sorption studies by these workers were undertaken between pH 7 and 8, and reported K_D values for Zn at salinities of 0, 19 and 22.5% were 4.6, 4.4 and 4.3 L/kg, respectively, and 3.9, 3.9 and 3.8, for Cu, respectively. The experimentally determined Cu, Pb and Zn K_D values reported here for pH 6 and pH 8 are of similar magnitude to *in-situ* values obtained for other moderately reducing (Eh +120 to +260 mV) sediments of the Moreton Bay region (Burton, personal communication; K_D values 2.0 to 4.0).

Table 3. Copper, Pb and Zn distribution coefficient ($\log_{10}K_D$) for each pH and salinity treatment calculated by Equation (2).

Metal	$\log_{10}K_D$ (L/kg) pH 4		$\log_{10}K_D$ (L/kg) pH 6		$\log_{10}K_D$ (L/kg) pH 8	
	5 ppt	30 ppt	5 ppt	30 ppt	5 ppt	30 ppt
			Sediment FS			
Cu	1.45	1.50	3.41	2.72	4.19	3.03
Pb	1.94	1.66	3.67	2.75	4.13	2.96
Zn	1.40	1.45	2.02	2.31	3.99	2.64
			Sediment MM			
Cu	2.44	2.10	3.61	3.10	3.95	3.84
Pb	2.85	2.22	3.92	3.07	4.43	3.54
Zn	1.67	1.51	2.09	2.49	4.22	3.28

The study reported here found pH to be the dominant factor affecting both the extent and rate of metal sorption by two contrasting estuarine sediments. For Cu and Pb, the estimated rate constants generally decreased in the order pH 8 > pH 6 > pH 4. The rate and magnitude of metal sorption was negatively affected by salinity due to (1) increased competition for the limited number of sorption sites, (2) reduced activity of aqueous trace metal species, and (3) ion-pair formation with artificial seawater anions. The MM sediment sorbed more of the added Cu and Pb compared to FS in all pH and salinity treatments, while Zn was only marginally affected. Zinc sorption behavior deviated from this expected sequence, and more study on the behavior of this metal under extreme pH and salinity conditions is required. Metal sorption rates and distribution coefficients were generally of the same magnitude as reported by other workers, and preferential sorption (involving both adsorption and precipitation mechanisms) of hydroxy-metal species represented a possible key sorption mechanism. The findings from this study indicate that at the pH of the estuarine environment of Moreton Bay (usually pH 7.5 to 8.0), a high proportion of metals added in urban runoff are likely to be sorbed very quickly by the sediments at their point of entry. However, resuspension of submerged sediments could translocate metal-contaminated sediments prior to settling. This aspect of metal availability, along with metal desorption, is currently being investigated in an associated study.

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